On the influence of agricultural additives to the availability of radium and uranium in tropical soils

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Abstract. It is already known that some agricultural practices can affect the concentration of natural and artificial radionuclides in soils and, consequently, the uptake of these elements by vegetables. Agricultural additives can change the original characteristics of the soil moisture, mainly pH and CEC (cation exchange capacity). The use of additives may modify the chemical forms of the natural radionuclides contained in soils and their behavior on soil. The radionuclide mobility may increase, resulting in migration of the radionuclide to deeper layers of the soil, or the mobility may decrease by absorbing on colloids and soil particles. Besides, as the uptake pattern depends on soil, plant and other environmental characteristics, the use of these additives may alter the uptake and consequently the contribution to internal dose by food consumption. In this study soil and vegetables samples were collected from farms at Nova Friburgo County, in the mountain region of the Rio de Janeiro state, Brazil. The soil of this region has to be limed for agricultural purpose. The ^{226}Ra, ^{228}Ra and ^{238}U concentration in the vegetables and its corresponding soils were determined as well the main chemical soil parameters (Ca, Mg, pH, organic matter, CEC, K, P, OM, etc). Correlation studies were carried out and showed a positive relationship between uranium content in plants and exchangeable Ca and Mg in soil, suggesting that liming supplies carbonate for the formation of uranium–carbonate complexes, increasing the ^{238}U availability for plants. On the other hand, the negative correlation between Ra contents in plants and the soil cations exchange capacity suggest that liming may promote a decreasing in the Ra uptake by plants, by adding cations to soil and, consequently, increasing the ion competition effects.

INTRODUCTION

Many soil characteristics govern the availability of nutrient elements to vegetable uptake, as cation exchange capability (CEC), pH, clay minerals content and organic matter. Some agricultural practices alter the cited and other characteristics of the soils and affect the speciation and uptake of nutrient and other elements as natural radionuclides [1,2].

The effects of the use of fertilizers on radionuclide behavior in soils have been reported in the literature. The use of phosphate fertilizers can also turn uranium species less available to uptake [3,4,5], once U will react with phosphate ion and precipitate. A lower concentration of U in grains from plants grown in fertilized fields than in grain from unfertilized fields was observed [6]. The high affinity of U for organic matter has also been recognized. Organic matter can be associated with higher levels of soluble humic acids which may form uranium complex and render it unavailable for plant uptake [7,8]. Add organic matter as organic manure may be another way to reduce U mobility [9,10,11].

In addition, some authors have shown that when adding lime to increase soil pH, the U and Ra isotopes will be more or less available to uptake. There are studies suggesting that the use of lime in acid soils to adequate the pH to the crops can reduce the availability of uranium by complexing this element with carbonates [12]. As lime is predominantly calcium and magnesium carbonate, liming also could lead to Ra co-precipitation with $BaCO_3$, and in consequence decrease Ra availability to plants [13, 14].

Data on plant uptake of radionuclides under natural field conditions are scarce and major literature data of natural radionuclide transfer to plants come from studies carried out on either soil in high background areas, mine tailing or pot and lysimeter experiments which all have high concentrations of radionuclides [5, 12, 13, 14]. These studies give only an approximation of the process occurring in normal agricultural systems and cannot reflect accurately the situation existing in low background environments [6,8,]. Therefore, studies under natural conditions in fields of Latosoils (an acidic soil that cover approximately 40% of the Brazilian territory) [15] can contribute for a better understanding of radionuclide uptake by plants in this type of environment.

The objective of this research was to investigate how the addition of fertilizers and lime and soil properties can affect the availability of uranium and radium isotopes in Brazilian soil and their uptake by plants.

MATERIALS AND METHODS

2.1 Samples collection and preparation

Composite samples of vegetables - lettuce (Lactuca sativa), representing leaf vegetables, and carrots (Daucus carota), representing root vegetables - and respective composite samples of soils and fertilizers were collected randomly at organic and conventional farms from the region of Nova Friburgo county, in the mountain region of Rio de Janeiro state, Brazil. This county is the major producer of leaf and root vegetables to consumption in the metropolitan region of Rio de Janeiro. The soils were collected at a depth of approximately 20 cm [3].

In order to determine ^{226}Ra and ^{228}Ra concentrations in soils samples by gamma spectrometry, aliquots of 300 g were stored in polyethylene containers, sealed and left to rest for a period of about 30 days to allow the re-establishment of secular equilibrium conditions between ^{226}Ra and its short-lived decay products in the samples.

Soil samples were air-dried, crushed and sieved in a 2 mm siev. The vegetable samples were washed twice, first with tap water and then with distilled water, peeled when necessary (in the case of carrots), air-dried and oven dried at 105 °C for 16 h. The samples were then ashed for 24 h in an oven at 450 °C to obtain around 30 g of ashes.

2.2 Soil Properties Analysis

The chemical analysis (pH and nutrient element data) of the soil samples were performed at the Soil Analysis Laboratories at EENF/Pesagro. All methods are described by the EMBRAPA [16].

2.3 ^{238}U and Radium Isotopes Analysis

The determination of radium isotopes in the soil samples were performed by gamma spectrometry with an HPGe detector: ^{226}Ra was determined through its daughter products ^{214}Pb (351 keV) and ^{214}Bi (609 keV) activities and ^{228}Ra was determined through the ^{228}Ac (911 keV) activity [17].

Radium determinations in vegetables, irrigation water and in the hydroponic nutrient solutions were performed by total alpha and beta countings. Radium was co-precipitated as $Ba(Ra,Pb)SO_4$ by adding H_2SO_4 and $BaCl_2$ to 1 l samples [18].

For uranium determination 1 g of ash vegetable or 1 g of soil was mineralized and the sample volume was completed to 20 ml with HNO_3 1 M. Uranium was extracted from 20 ml of sample in HNO_3 1M by 0.1M trioctylphosphine oxide in cyclohexane. Subsequently, ^{238}U was determined by fluorimetric analysis of the organic phase. The method is based on the comparison of the fluorescence of a known standard with a

sample of similar but unknown concentration in LiF/NaF fluorescence-enhancing reagent [19].
As the ^{238}U and radium isotopes analytical methods are used in a routine basis at IRD laboratories, their performances are routinely tested through participation in inter-laboratory exercises organized by different international organizations, such as EML/USDOE, New York, MAPEP/RESL/USDOE, Idaho Falls, and the PNI/IRD/CNEN, Rio de Janeiro [20].
The distribution of the data set was verified by plotting the cumulative frequency curve on normal probability paper [20, 21]. The result showed that the concentrations of all variables, except by pH values, were better represented by the log-normal distribution and the central tendency is then represented by the geometric mean [1, 22, 23]. The geometric mean and the geometric standard deviation were used for the comparison of means and standard deviations by the t-test [23]. The data association tests were performed with the data log-transformed [22].

3. RESULTS AND DISCUSSION

3.1. Soil characteristics

The soil pH and chemical characteristics are given in table 1. The soils of Nova Friburgo county are described as red–yellow dystrophyc Latosols [24] and the texture are sandy–clay–loam.
No significant statistical difference was found between the nutrient status of the soils from conventional and organic farms. The nutrient data of the soils show that the soils are constantly fertilized, with suitable levels of P (>40 mg.kg-1) and K (>0.30 cmol.kg-1). Most of the soils used for carrot cultivation are acidic (C1Ca, C2Ca, C3Ca, C4Ca, O1Ca and O2Ca) and the values were lower than the recommended range for pH value for the vegetable cultivation the levels of exchangeable Al^{+3} are high.

Table 1. Soil characteristics**.**

Agricultural practice	pH_{H2O}	Ca	Mg	Al	K	CEC	Organic matter (OM) (g.kg^{-1})	P (mg.kg^{-1})
		cmol.kg^{-1}						
C1L	5.10	2.5	1.8	0.2	0.80	13.5	20.7	70
C2L	5.68	4.0	2.0	<0.1	0.40	11.3	25.9	63
C3L	5.96	5.6	3.2	<0.1	0.46	13.3	20.7	81
C4L	5.94	5.5	3.2	<0.1	0.47	1.03	21.0	80
01L	6.76	6.5	3.1	<0.1	0.40	12.5	20.7	78
02L	6.42	7.3	2.3	<0.1	0.63	15.5	10.3	77
03L	5.87	3.0	1.3	<0.1	0.37	9.4	32.8	79
04L	6.54	4.9	1.7	<0.1	0.40	10.3	22.4	42
C1Ca	4.99	3.7	1.3	0.2	0.50	13.1	22.4	78
C2Ca	4.70	1.8	1.1	0.3	0.37	10.5	32.7	74
C3Ca	4.90	1.5	1.0	0.7	0.40	11.4	25.9	75
C4Ca	4.74	1.5	0.6	0.6	0.4	10.5	22.4	73
O1Ca	5.03	1.9	0.8	0.4	0.30	12	15.5	42
O2Ca	5.04	1.8	0.9	0.4	0.30	12	15.5	42
03Ca	6.42	6.0	1.7	<0.1	0.53	12.3	22.4	74
O4Ca	5.61	4.5	1.3	<0.1	0.40	10.1	22.4	68
O5Ca	5.63	4.4	1.3	<0.1	0.40	10.0	22.4	69

C = conventional; O= organic; L= Lettuce; Ca= carrot

3.2 Radionuclide concentrations in soils

The geometric mean, geometric standard deviation and range of uranium and radium concentrations in the 17 soils of the lettuce and carrot farms are given in table 2 and are within the range for normal background values reported for Brazilian soils [27] and worldwide [28]. They are reported as an average, since they don't differ on the average test T. All soils are slightly depleted in uranium when compared to radium, notwithstanding fertilization type.

Statistical association analysis showed no relation between the concentration of radionuclides in the soil with the measured soil properties, i.e., pH; exchangeable Ca^{+2}, Mg^{+2}, Al^{+3}, K+ and P; organic matter content; and cation exchange capacity (table 1). No statistical significant difference was observed between the uranium and radium isotope concentrations in organic and conventional crop soil samples ($p < 0.05$) from the different types of vegetables.

Table 2. Geometric means and geometric standard deviations (δ) of ^{226}Ra, ^{228}Ra and ^{238}U concentrations (Bq.kg^{-1}) in soil samples.

Soil sample	N	^{26}Ra	^{228}Ra	^{238}U
Conventional Lettuce	4	48 (δ=1.5)	72 (δ=1.5)	50 (δ=1.9)
Organic Lettuce	4	40 (δ=1.5)	76 (δ=1.4)	48 (δ=1.4)
Conventional Carrot	4	41(δ=1.1)	54 (δ=1.4)	23 (δ=1.5)
Organic carrot	5	46 (δ=1.1)	51(δ=1.3)	28 (δ=1.3)

3.3 Radionuclide concentrations in vegetable samples

The geometric mean and geometric standard deviations and the range of radionuclides in vegetables are presented in Table 3. They are too reported as an average, since they don't differ on the average test T. Among the radionuclides analyzed, the obtained results showed the same trend usually observed in Brazilian environmental samples: ^{238}U presented the lowest concentrations, whereas ^{228}Ra showed the highest concentrations [29].

In a general way, the levels of radium isotopes (^{226}Ra and ^{228}Ra) in the vegetables were higher in carrots (0.27 and 0.45 Bq.kg^{-1} fresh) than lettuce (0.05 and 0.08 Bq.kg^{-1} fresh), while uranium content followed the inverse order: lettuce (0.018 Bq.kg^{-1} fresh) >carrots (0.010 Bq.kg^{-1} fresh), and this difference in the concentrations among the vegetables is an outcome of differential uptake of radionuclides by plant species [8].

Comparing the data of vegetables from the different farming management systems, no significant differences were found between the concentration values of ^{226}Ra and ^{228}Ra in lettuce, carrots, and beans organically grown with those conventionally grown [30]. The same trend was observed for the data set of ^{238}U concentrations in the conventionally and organically grown lettuce and carrots.

Table 3. Geometric means and geometric standard deviations (δ) for ^{226}Ra, ^{228}Ra and ^{238}U, concentrations values in vegetables samples from different agriculture managements (in Bq. kg$^{-1}_{dry}$).

Vegetable	Crop Management	N	^{226}Ra	^{228}Ra	^{238}U
Lettuce	conventional	4	1.54 (δ=1.54)	2.36 (δ=1.75)	0.70 (δ=2.17)
Lettuce	organic	4	1.38(δ=1.83)	2.47 (δ=2.39)	0.52 (δ=1.87)
Carrot	conventional	3	2.19 (δ=1.78)	2.62 (δ=2.10)	0.05 (δ=1.27)
Carrot	organic	4	2.75 (δ=1.46)	5.80 (δ=1.39)	0.06 (δ=1.70)

3.4 Relationship between radionuclide concentrations in plant and soil properties

3.4.1. Uranium concentration in plants and soil properties

The difference in uranium concentration in conventional and organic farming systems may be related more to uranium's higher retention by organic matter organically fertilized soil than to availability (caused by phosphate fertilizer input or by the lower pH value) in conventionally fertilized soil. Correlation analysis was carried out between the content of U in each vegetable type and the content of the radionuclide in the soil.

As has been observed in several studies of soil to plant transfer, no correlation was found between the radionuclide content in vegetables with the levels of the radionuclide in soil [1,7 10]. Most measured soil variables were not correlated with U content in vegetables. However, both lettuce and carrot crops exhibited a very weak association ($p< 0.20$) between uranium content in vegetables and the exchangeable Ca^{+2} and Mg^{+2} in soil. When all vegetables were pooled together, a significant correlation was found for Ca^{+2} ($p < 0.05$), for Mg^{+2} ($p <0.01$) and for the sum Ca^{+2} + Mg^{+2} ($p< 0.01$). Figure 1 shows the relationship between the measurable values of 238U in plant and the exchangeable Ca+2 of soil. Information regarding influence of exchangeable Ca and Mg in soil on U uptake by plants is scarce and a positive effect of these cations on U uptake by plant cannot be disregarded. Vandenhove et al. [2] mentioned a negative correlation between the soil solution partition coefficient (Kd) of U and exchangeable Ca and Mg in soil and a positive correlation between the exchangeable Ca^{+2} and U TF. However, the correlation may possibly be associated to the use of dolomite ($CaCO_3.MgCO_3$) as lime in the Nova Friburgo region. An increase of U availability for plants has been attributed to carbonate–uranyl complexes, which started to be formed in solutions at pH 4.2 and become the predominant inorganic U species above pH 6–7 [32]. In agreement with this Tyler and Olsson [13] observed an increase of U uptake with the increase of pH caused by soil liming with calcium carbonate) and formation of carbonate–uranyl complexes. Although no correlation between U and soil pH was found in our studies, a significant correlation was found between exchangeable Ca and pH and Mg and pH ($p< 0.01$ and $p <0.05$, respectively).

3.4.2. Radium isotope concentrations in plant and soil properties

Ra–carbonate complexes will be present only in concentrated saline solutions and will only be significant in pH >10.25 [32]. Furthermore, liming raises the content of Ca and Mg in soil and increases the cation competitive effects for adsorptive surfaces of roots. However, its concentration in soil solutions is much lower than the other alkaline metals and in the presence of high alkaline cation concentration, the uptake of Ra may be suppressed. As a result, increased exchangeable Ca in soil is reported to decrease the radium uptake [1]. Nevertheless, in this research, no correlation was found between ^{226}Ra and ^{228}Ra in vegetables with exchangeable cations in soil, which is compatible with the results obtained by [12].

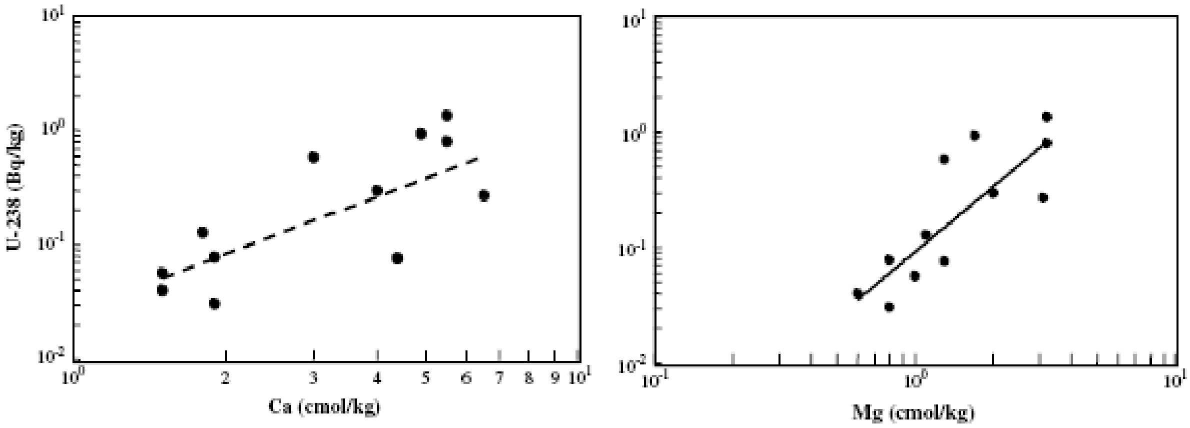

Figure 1. Relationship between the measurable values of ^{238}U in vegetables and the exchangeable Ca^{2+} and Mg^{2+} in soils.

Instead, a weak inverse association was found between the content of ^{226}Ra and the cation exchange capacity (CEC) of soil for lettuce ($p < 0.10$) and for carrot ($p < 0.15$). When all vegetables are pooled together a greater inverse association was found ($p < 0.05$) as can be seen in the figure 2. This result is in agreement with the association between CEC in soil and Ra content in vegetables observed by Vandenhove and Van Hees [2]. On the other hand, a very weak association was found for ^{228}Ra with regards to individual vegetables ($p < 0.20$) as well as for the pool of vegetables ($p < 0.10$). The high measurement error associated with ^{228}Ra analysis might influence the observed difference between ^{226}Ra and ^{228}Ra observed in the correlation studies. The alpha–beta counting method employed for this study is very sensitive and allows for the simultaneous determination of ^{226}Ra and ^{228}Ra, but the relatively high background levels of beta radiation and interference from ^{226}Ra, increase the ^{228}Ra measurement uncertainties [33]. The error of measurements of ^{226}Ra in the obtained results varied from 8 to 20%, while the 228Ra associated errors ranged from 9 to 43%.

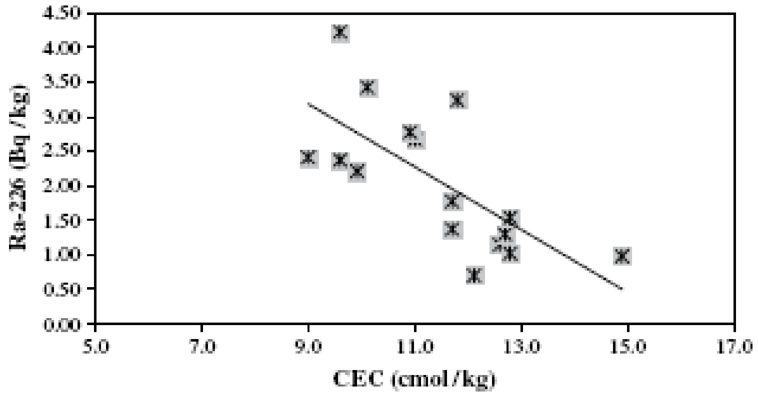

Figure 2. Variation of ^{226}Ra concentration in lettuce and carrots and the cation exchange capacity of soil.

4. CONCLUSIONS

No differences in the concentration of radium and uranium were found in vegetables from either organic or conventional management systems that could be imputed to phosphate fertilizers.
As the soil in organic management contains a higher organic matter level, the U retention in this soil would be higher than in the conventional management system.
In general, the uranium and radium concentrations in the chemical fertilizers were relatively low and the values found fall within the lower range of the values reported in the literature. Because of the high amounts used, organic fertilizer can add more Ra to soil than fertilizers, whereas phosphate fertilizer adds more U to soil. Nevertheless, the amount of radionuclides supplied by fertilization is less than 0.5% of the total level of

the radionuclides in soil. However, the increase in activity due to fertilization is not significant enough to be detectable; given the sensibility of the methods of determination used.
Relationships between uranium content in plants and exchangeable Ca and Mg in soil were found, leading to the assumption that liming supplies carbonate for the formation of uranium–carbonate complexes, increasing the U availability for plants. Ra in vegetables was inversely correlated to the CEC (cation exchange capacity) of soil, which might be due to a reduction of radium uptake by plants as a result of the competition effect.
In conclusion, by supplying carbonate and cations to soil, liming may cause an increase of U and a decrease of radium uptake by plants.

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